An Electron Spin Resonance Study of 1-Alkylthioallyl, 3-Alkylthiopropynyl, and Alkylthioalkyl Radicals: an Examination of Spin Delocalization by Alkylthio Groups

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E.s.r. spectra have been recorded for $CH_2CH\dot{C}HSBu^t$ and $HC\equiv C\dot{C}HSBu^t$. The hyperfine splitting constants indicate that considerable spin density is delocalized onto the SBu^t group. This group is a more effective acceptor of spin than alkyl, hydroxy, or alkoxy substituents, and comparable with that of an ethynyl substituent. The barrier to rotation about the C_α–S bond in $AdS\dot{C}H_2$ is greater than that about the C_α–O bond in $AdO\dot{C}H_2$ as a consequence of greater spin delocalization onto sulphur than onto oxygen. The mechanism of reaction of t-butoxyl radicals with sulphides is discussed. The $Bu^tS\dot{C}HCH_2OCH_3$ radical exists in an eclipsed conformation whereas $Bu^tS\dot{C}HCH_2Ph$ and $CH_3O\dot{C}HCH_2Ph$ prefer staggered conformations.

We have recently made an e.s.r. study of 1-aminoallyl, $R_2N\dot{C}HCH=CH_2$, and 3-aminopropynyl radicals, $R_2N\dot{C}HC\equiv CH$, and showed that the hyperfine splitting constants of all the hydrogens of the allyl and propynyl moieties were considerably less than in the parent allyl and propynyl radicals indicating a high degree of electron delocalization onto the amino groups.[1] In agreement with these observations, it has been reported that the stabilization energies of α-aminoalkyl radicals are comparable to those of the allyl radicals.[2,3] In this communication we report a similar e.s.r. study on t-butylthioallyl, $Bu^tS\dot{C}HCH=CH_2$, and t-butylthiopropynyl radicals, $Bu^tS\dot{C}HC\equiv CH$, in an attempt to get some idea of the spin delocalizing ability of t-butylthio groups relative to other groups, particularly alkoxy groups. We have also examined a number of other α-alkylthioalkyl radicals.

The magnitude of the α-proton hyperfine coupling constants in a series of thioalkoxyalkyl radicals, $RSCH_2\cdot$, is smaller than for the corresponding α-alkoxyalkyl radicals, $RO\dot{C}H_2$, and the barrier to rotation about the C_α–S bond in $CH_3S\dot{C}H_2$ is greater than that about the C_α–O bond in $CH_3OCH_2\cdot$ suggesting that sulphur is more effective at delocalizing unpaired spin than oxygen.[4] There has, however, to be considerable doubt as to the significance of these results because of the differing degrees of planarity at the radical centre in the two classes of radical: the oxygen radicals are appreciably less planar than their sulphur analogues.[5,6]

In this study we chose to examine alkoxy- and thioalkoxy-substituted allyl and propynyl radicals, $RX\dot{C}HCH=CH_2$ and $RX\dot{C}HC\equiv CH$ (X=O and S), as it is probable that the radical centres in these radicals are planar. It has been reported that aryl groups in α-aryl-α,α-dioxygen-substituted radicals, *e.g.* $Ph\dot{C}(OMe)_2$, promote planarity at the radical centre[7] and it can be anticipated that the vinyl and ethynyl groups will similarly promote planarity in the radicals we have chosen to study. The one reported study on radicals of this type, namely $PhX\dot{C}HCH=CH_2$,[6] was not particularly definitive in that the radicals existed as mixtures of the *endo*- and *exo*-conformers thus making assignment of coupling constants impossible. The results did, however, indicate that the extent of delocalization of unpaired spin onto sulphur was greater than onto oxygen.

Results and Discussion

E.s.r. Spectra of 1-t-Butylthioallyl and 3-t-Butylthiopropynyl Radicals.—1-t-Butylthioallyl and 3-t-butylthiopropynyl radicals were generated in the cavity of an e.s.r. spectrometer by hydrogen abstraction from the thioether precursors with t-butoxyl radicals. Cyclopropane was used as a solvent for low-temperature studies and di-t-butyl peroxide for temperatures above 240 K. t-Butyl sulphides were used to ensure that hydrogen abstraction took place only at the allylic or propargylic position. Preliminary experiments with allyl ethyl sulphide indicated that hydrogen abstraction took place in the ethyl group as well as at the allylic position.

$$(Bu^tO)_2 \longrightarrow 2Bu^tO\cdot \qquad (1)$$

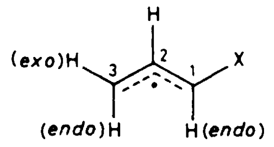
$$Bu^tO\cdot + Bu^tSCH_2CH=CH_2 \longrightarrow Bu^tOH + Bu^tS\dot{C}H\text{–}CH=CH_2 \qquad (2)$$

$$Bu^tO\cdot + Bu^tSCH_2C\equiv CH \longrightarrow Bu^tOH + Bu^tS\dot{C}H\text{–}C\equiv CH \qquad (3)$$

The e.s.r. spectrum obtained from reaction of allyl t-butyl sulphide with t-butoxyl radicals at 220 K indicated that two radicals were formed. The e.s.r. spectrum of each radical consisted of four doublets characteristic of α-substituted allyl radicals. (The coupling constants of the major radical were 0.36, 1.15, 1.19, and 1.23 mT and of the minor radical 0.37, 1.17, 1.19, and 1.25 mT).[8] These were presumably the *endo*- and *exo*-1-t-butylthioallyl radicals with the *exo*-radical being the more abundant species. The splitting constants were assigned by analogy with studies on a number of α-substituted allyl radicals by Edge and Kochi.[8] The significant feature of the spectra is that the coupling constants with H-1, H-3-*exo*, and H-3-*endo* are substantially lower than for other reported α-substituted allyl radicals with the exception of α-aminoallyl radicals (see Table 1).

The e.s.r. spectrum of the 3-t-butylthiopropynyl radical, $Bu^tS\dot{C}HC\equiv CH$, consists of a doublet of doublets. The coupling constants at H-1 and H-3 are significantly lower than in most substituted propynyl radicals with the exception of 3-amino-

Table 1. E.s.r. parameters for *exo*-1-substituted allyl radicals



	Coupling constants (mT)					
X	*T*/K	*a*(H-1-*endo*)	*a*(H-2)	*a*(H-3-*exo*)	*a*(H-3-*endo*)	Ref.
H	143	1.390	0.406	1.481	1.390	9
CH_3	163	1.383	0.385	1.478	1.383	9
Cl	298	1.39	0.41	1.48	1.39	10
OH	231	1.315	0.366	1.423	1.315	8
OCH_3	180	1.305	0.335	1.415	1.330	11
OBu^t	171	1.307	0.291	1.365	1.307	8
SBu^t	220	1.150	0.360	1.231	1.193	This work[a]
	156	1.15	0.37	1.24	1.22	This work[b]
$SiMe_3$	149	1.249	0.369	1.420	1.249	8
CO_2Me	180	1.365	0.367	1.365	1.280	11
CN	183	1.425	0.363	1.310	1.230	12
NH_2	240	1.16	0.24	1.25	1.21	1
$CH{=}CH_2$(*trans*)	233	1.16	0.33	1.04	0.96	13
C≡CH	175	1.38	0.36	1.15	1.06	14

[a] In excess of $(Bu^tO)_2$ as solvent. [b] In cyclopropane as solvent

Table 2. E.s.r. parameters of 3-substituted propynyl radicals, $HC{\equiv}C\dot{C}HX$

	Hyperfine splittings (mT)						
X	*T*/K	*a*(H-1)	*a*(H-3)	*a*(C-1)	*a*(C-2)	*a*(C-3)	Ref.
H	153	1.27	1.89	2.29	1.81	3.39	15,16
CH_3	162	1.178	1.870				15
$OSiMe_3$		1.07	1.83	2.14	1.76	2.71	16
SBu^t	153	0.945	1.53	1.90	1.45	2.66	This work[a]
	233	0.940	1.53				This work[b]
C≡CH	160	0.95	1.66				14
$CH{=}CH_2$(*trans*)	175	0.84	1.38				14
NH_2	370	0.81	1.47				1
$NHBu^t$	137	0.80	1.37				1

[a] In cyclopropane as solvent. [b] In excess of $(Bu^tO)_2$ as solvent.

and 3-alkylamino-propynyl and -pentenynyl radicals (see Table 2). The results once again indicate clearly that the t-butylthio group is very effective at delocalizing spin. The values of the hyperfine splitting constants would seem to suggest that the t-butylthio group has a similar spin delocalizing ability as an ethynyl group but less than that of an amino or an alkylamino group.

The spectrum of the 3-t-butylthiopropynyl radical was sufficiently intense to enable the ^{13}C coupling constants to be determined. The magnitudes of these coupling constants (Table 2) again indicate that the t-butylthio group is effective at delocalizing unpaired spin and that it is much more efficient than the trimethylsilyloxy group.[16]

Examination of the data presented in Table 2 indicates that the ratio of the spin density at C-1 to that at C-3 varies with the nature of the substituent X. Experiments are in hand to elucidate the origin of this effect.

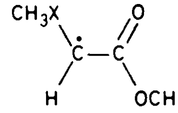
E.s.r. Spectra of $MeX\dot{C}HCN$ ***and*** $MeX\dot{C}HCO_2Me$ ***Radicals.***—We have also examined the e.s.r. spectra of the radicals derived from methoxy- and thiomethoxy-acetonitriles, $MeXCH_2CN$ (X = O and S), and from methyl methoxy- and thiomethoxy-acetates $MeXCH_2CO_2Me$. The derived radicals $MeX\dot{C}HCN$ and $MeX\dot{C}HCO_2Me$ are isoelectronic with the substituted propynyl and allyl radicals studies above and can likewise be expected to be planar. In both sets of compounds the hyperfine splitting constant for the α-proton was lower in the thiomethoxy compound than in the methoxy compound (see Table 3) These results thus similarly indicate that a thioalkoxy group is significantly more effective at delocalizing unpaired spin than an alkoxy group and parallel those obtained from a study of the ^1H e.s.r. spectra of $Bu^tO\dot{C}HCN$ [*a*(1 H) 1.74 mT] and $Bu^tS\dot{C}HCN$ [*a*(1 H) 1.48].[17]

E.s.r. Spectra of Radicals derived from $Bu^tSCH_2CH_2CH{=}CH_2$, $Bu^tSCH_2CH_2Ph$, *and* $Bu^tSCH_2CH_2CH_2Ph$.—An attempt to compare the spin delocalizing ability of alkylthio groups with that of vinyl and phenyl groups was made by examining the reactions of t-butoxyl radicals with $Bu^tSCH_2CH_2CH{=}CH_2$ and $Bu^tSCH_2CH_2Ph$ in the cavity of an e.s.r. spectrometer. Contrary to our expectations the radicals obtained were the t-butylthioalkyl radicals, $Bu^tS\dot{C}HCH_2CH{=}CH_2$ and $Bu^tS\dot{C}HCH_2Ph$. The spectra of both radicals consisted of a

Table 3. E.s.r. parameters of $RX\dot{C}HCN$ and $RX\dot{C}HCO_2Me$ radicals[a]

		Hyperfine splittings (mT)				
Radical	T/K	a(α-H)	a(γ-H)	a(δ-H)	a(N)	Ref.
$CH_3O\underset{\cdot}{C}HCN$	240	1.84	0.265		0.350	This work
$CH_3S\underset{\cdot}{C}HCN$	240	1.51	0.41		0.30	This work
$Bu^tO\underset{\cdot}{C}HCN$	299	1.744		0.022	0.315	15
$Bu^tS\underset{\cdot}{C}HCN$	298	1.482			0.268	17
$CH_3O\dot{C}HCO_2CH_3$[b]	215	1.762	0.285	0.159		17
		1.740	0.282	0.112		
$CH_3S\dot{C}HCO_2CH_3$[b]	240	1.50	0.40			This work
		1.50	0.41			

[a] Spectra recorded in excess of $(Bu^tO)_2$ as solvent. [b] Radicals produced as a mixture of conformers (**1** and **2**; X = O and S).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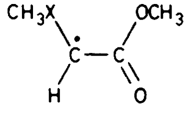

(**2**)

Table 4. E.s.r. parameters of radicals derived from sulphides and an ether

			Hyperfine splittings (mT)		
Substrate	Radical	T/K	a(α-H)	a(β-H)	a(γ-H)
$PhCH_2CH_2SBu^t$	$PhCH_2\dot{C}HSBu^t$	215[a]	1.60(1H)	1.775(2H)	
		295[a]	1.59(1H)	1.72(2H)	
$PhCH_2CH_2CH_2SBu^t$	$PhCH_2CH_2\dot{C}HSBu^t$	244[a]	1.57(1H)	1.57(2H)	0.05(2H)
		320[a]	1.55(1H)	1.62(2H)	0.05(2H)
$CH_2{=}CHCH_2CH_2SBu^t$	$CH_2{=}CHCH_2\dot{C}HSBu^t$	215[a]	1.66(1H)	1.66(2H)	
		315[a]	1.60(1H)	1.69(2H)	
$Bu^tSCH_2CH_2CH_2SBu^t$	$Bu^tS\dot{C}HCH_2CH_2SBu^t$	240[a]	1.67(1H)	1.59(2H)	0.07(2H)
		260[a]	1.67(1H)	1.62(2H)	0.07(2H)
$CH_3SCH_2CH_2SCH_3$	$\dot{C}H_2SCH_2\underset{\cdot}{C}H_2SCH_3$	240[a]	1.70(2H)		0.18(2H)
$CH_3OCH_2CH_2SBu^t$	$CH_3OCH_2\dot{C}HSBu^t$	220[b]	1.57(1H)	1.02(2H)	
	(major)	220[b]	1.66(2H)		0.19(2H)
	$\dot{C}H_2OCH_2CH_2SBu^t$	280[c]	1.57(1H)	1.11(2H)	
	(minor)				
	$\underset{\cdot}{C}H_3OCH_2\dot{C}HSBu^t$				
$CH_3OCH_2CH_2SCH_3$	$\dot{C}H_2SCH_2CH_2OCH_3$	220[a]	1.57(1H)		0.18(2H)
			1.67(1H)		
$PhCH_2CH_2OCH_3$	$PhCH_2\dot{C}HO\underset{\cdot}{C}H_3$	245[a]	1.35(1H)	1.94(2H)	0.15(3H)
	$PhCH_2\underset{\cdot}{C}H_2O\dot{C}H_2$	245[a]	1.63(2H)		0.18(2H)
	$PhCH_2\dot{C}HOCH_3$	290[a]	1.35(1H)	1.91(2H)	0.15(3H)

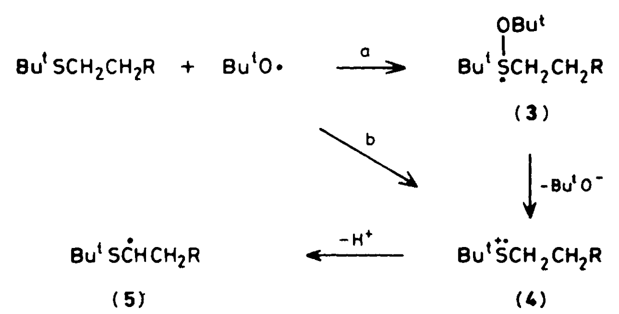
[a] In $(Bu^tO)_2$ as solvent. [b] In PhMe as solvent. [c] In $PhBu^t$ as solvent.

doublet of triplets (see Table 4). There was no evidence whatsoever of the formation of any of the allylic or benzylic radicals, $Bu^tSCH_2\dot{C}HCH{=}CH_2$ and $Bu^tSCH_2\dot{C}HPh$. These two radicals are, however, β-alkylthioalkyl radicals which are known to undergo facile fragmentation,[18] *e.g.* $Bu^tSCH_2\dot{C}HPh \longrightarrow Bu^tS\cdot + CH_2{=}CHPh$.

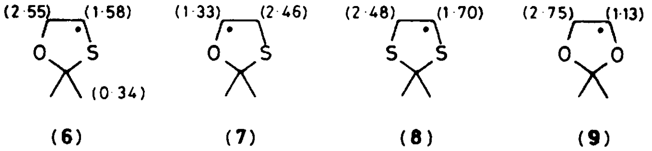
We thus decided to examine the reaction of t-butoxyl radicals with $Bu^tSCH_2CH_2CH_2Ph$, which was expected to give $Bu^tS\dot{C}HCH_2CH_2Ph$ and/or $Bu^tSCH_2CH_2\dot{C}HPh$: this latter radical would not undergo ready β-scission, and hence, if formed, should be readily observable. Once again the only one which could be detected was the t-butylthioalkyl radical, $Bu^tS\dot{C}HCH_2CH_2Ph$. The e.s.r. spectrum consisted of a doublet of triplets with a further small splitting due to the γ-protons, a(1 H) 1.55, a(2 H) 1.62, a(2 H) 0.065 mT. This confirms that abstraction occurs mainly on the carbon α to the sulphur.

Mechanism of Reaction of Sulphides with t-Butoxyl Radicals.—The above result seems to be at variance with what might be expected on thermodynamic considerations. The e.s.r. data presented in Tables 1 and 2 indicate that an alkylthio group is less efficient at delocalizing unpaired spin than a vinyl group. Gilbert *et al.* postulated that the reaction of methionine with a hydroxyl radical proceeds *via* sequential formation of a hydroxy adduct at sulphur and a sulphur-centred radical cation.[19] A similar pathway may well be involved in the reaction of sulphides with t-butoxyl radicals with initial formation of the radical adduct (**3**) followed by loss of t-butoxide to give the sulphur-centred radical cation (**4**) and final proton loss to give the observed α-t-butylthioalkyl radical (**5**) (Scheme; path a). A precedent for the first step in this process occurs in the reaction of t-butoxyl radicals with thietane: in that case the resultant sulphur-centred radical undergoes ring opening to give $Bu^tOSCH_2CH_2CH_2\cdot$.[20] We observed the same process in the reaction of methylthiyl radicals with thietane. The radical cation (**4**) could also be formed directly from the sulphide in an electron-transfer process (Scheme; path b).

We also investigated the reaction of $Bu^tO\cdot$ with $PhCH_2CH_2$-



Scheme.



E.s.r. parameters of radicals derived from 2,2-dimethyl-1,3-oxathiolane, -1,3-dithiane, and -1,3-dioxolane (mT)

OCH_3. The resulting e.s.r. spectrum indicated that $PhCH_2CH_2OCH_2\cdot$ and $PhCH_2\dot{C}HOCH_3$ radicals were formed (in a ratio of *ca.* 1:2 at 245 K and 1:3 at 290 K). The formation of these radicals and the absence of any of the benzylic radical $Ph\dot{C}HCH_2OCH_3$ is also consistent with electron-transfer mechanism.

E.s.r. Spectra of Radicals derived from β-Alkoxyalkyl Alkyl Sulphides.—We have also examined the nature of the radicals generated in reactions of t-butoxyl radicals with β-alkoxyalkyl alkyl sulphides, $ROCH_2CH_2SR'$, to explore the relative spin-withdrawing efficiences of alkoxy and thioalkoxy groups. Two radicals could be detected in the reaction of $Bu^tSCH_2CH_2OCH_3$ with t-butoxyl radicals at 220 K. The major component was identified as $Bu^tS\dot{C}HCH_2OCH_3$ [a(1 H) 1.58, a(2 H) 1.02 mT] and the minor component as $Bu^tSCH_2CH_2O\dot{C}H_2$ [a(2 H) 1.65, a (2 H) 0.19 mT]. The minor radical was relatively less abundant at higher temperatures (280 K). None of the other possible radical $Bu^tSCH_2\dot{C}HOCH_3$, could be detected, possibly because it would undergo facile β-scission to $Bu^tS\cdot$ and $CH_3OCH{=}CH_2$.

In support of this postulate, we observed only one radical, namely $\dot{C}H_2SCH_2CH_2SCH_3$, in the reaction of $Bu^tO\cdot$ with $CH_3SCH_2CH_2SCH_3$. The e.s.r. spectrum consisted of a double doublet at 220 K indicating that the two α-protons were non-equivalent due to restricted rotation about the $\dot{C}H_2$–SR bond. This behaviour has been previously observed for other radicals of type $\dot{C}H_2SR$.[4,21,22] Each component of this double doublet was further split into a triplet as a result of coupling with the γ-protons (see Table 3). None of the isomeric radical $CH_3S\dot{C}HCH_2SCH_3$ was observed as this presumably would undergo facile β-scission. It is interesting to note that $CH_3SCH_2CH_2CH_2SCH_3$ was reported to give both $\dot{C}H_2SCH_2CH_2CH_2SCH_3$ and $CH_3S\dot{C}HCH_2CH_2SCH_3$. Neither of these is a β-thioalkyl radical.[23] The major radical obtained from $CH_3SCH_2CH_2OCH_3$ was $\dot{C}H_2SCH_2CH_2OCH_3$. The α-protons were again non-equivalent (see Table 4). The e.s.r. spectrum also indicated that $CH_3S\dot{C}HCH_2OCH_3$ and $CH_3SCH_2CH_2OCH_2\cdot$ were also formed in lesser amounts but complete analysis of the spectrum was not possible.

E.s.r. Spectra of the Radicals derived from 2,2-Dimethyl-1,3-thioxolane.—We also examined the reaction of $Bu^tO\cdot$ with 2,2-dimethyl-1,3-thioxolane. This gave rise to a mixture of two radicals in the ratio 10:1. The major component is believed to be the α-thio radical (**6**) and the minor component the α-oxo radical (**7**) by analogy with the behaviour of 1,4-thioxane which gave only the α-thio radical.[4] The hyperfine splittings of the α-thio radical (**6**) more closely resemble those of the radical (**8**) than (**9**): these radicals were derived from 2,2-dimethyl-1,3-dithiolane and 2,2-dimethyl-1,3-dioxolane, respectively. The e.s.r. spectrum of (**6**) shows δ-coupling to the protons of the *gem*-dimethyl group. No similar coupling was observable in (**8**) or (**9**).

It is interesting to note that the β-thioalkyl radicals (**6**) and (**8**) and also the radical from 1,4-dithiane are readily observable unlike their acyclic analogues.[4] Two reasons could be advanced for this difference. First on purely entropic considerations the cyclic radical may well be favoured over its ring-opened derivative, and second, in the cyclic system stereoelectronic considerations possibly act against facile ring opening.

Table 5. Barriers to rotation about CH_2–O and CH_2–S bonds in $RO\dot{C}H_2$ and $RSCH_2$ radicals

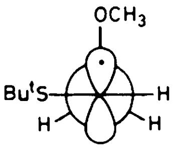
Radical	log (ν_0/s^{-1})	E_a/kJ mol^{-1}	Ref.
$HOCH_2\cdot$	12.6	19.2	24
$CH_3OCH_2\cdot$	12.6	22.2	4,24
$Bu^tSCH_2CH_2OCH_2\cdot$	13.0 ± 0.1	23.5 ± 1.3	This work
$Bu^tSCH_2CH_2OCH_2\cdot$	13.0 ± 0.1	17.7 ± 1.0[a]	This work
$Bu^tOCH_2\cdot$	13.1 ± 0.1	18.6 ± 0.9	This work
$AdOCH_2\cdot$	12.5	25.4 ± 2.0	4
$Bu^tSCH_2\cdot$	12.6 ± 0.2	26.3 ± 0.9	This work
$AdSCH_2\cdot$		> 30	4
$CH_3SCH_2\cdot$			

[a] A value of 20 ± 2 kJ mol^{-1} has previously been reported.[20]

Barriers to Rotation about CH_2–X *Bonds in* $\dot{C}H_2$–XR *Radicals.*—The e.s.r. spectrum of the radical $Bu^tSCH_2CH_2OCH_2\cdot$ showed exchange broadening of the central lines. Below *ca.* 210 K non-equivalent α-hydrogens (a 1.62 and 1.77 mT at 170 K) were observed and above this temperature the hydrogens became equivalent. The line broadening at coalescence and above was analysed by relaxation matrix theory using the method of Chen *et al.*[24] The rate constants for rotation about the $\dot{C}H_2$–OR bond were plotted in Arrhenius form and the activation energy and pre-exponential factor are recorded in Table 5.

The Arrhenius parameters are close to those determined previously for rotation about $CH_2\cdot$OR bonds in $HOCH_2\cdot$[25] and $CH_3OCH_2\cdot$.[4,25] The barrier to rotation in $Bu^tO\dot{C}H_2\cdot$ has been roughly estimated previously,[21] but we have accurately determined the Arrhenius parameters by simulation of the e.s.r. spectra in the temperature range 135—185 K.

For purposes of comparison the e.s.r. spectra of $AdOCH_2\cdot$, derived from 1-methoxyadamantane, and $AdSCH_2\cdot$, derived from the thio-substituted analogue, were examined. Both radicals showed double doublet structure at low temperature (1.69 and 1.86 mT for $AdOCH_2\cdot$ and 1.54 and 1.66 mT for $AdSCH_2\cdot$) the α-hydrogens becoming equivalent at *ca.* 155 and 250 K, respectively. The exchange-broadened spectra were simulated using a modified version of Heinzer's program,[26] excellent correspondence between observed and calculated spectra being obtained. The Arrhenius parameters derived for the two bond rotations are compared with literature data in Table 5. The rate constants for bond rotation in $AdS\dot{C}H_2\cdot$ were also calculated using the method of Chen *et al.*[24] and results essentially identical to the simulation method were



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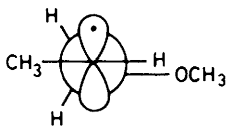

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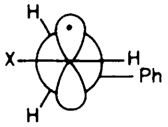

(12)

obtained. The experimental pre-exponential terms are all close to 10^{13} s^{-1}, the value expected for a simple bond rotation, and this lends confidence to the reliability of the results.

Comparison of the barriers in the thioalkoxymethyl and alkoxymethyl radicals with the same alkyl substituents, *i.e.* Bu^{t}SCH$_2$· and Bu^{t}OCH$_2$· and AdSCH$_2$· with AdOCH$_2$· (Table 5) shows that in each case the barrier about the S–CH$_2$ bond is greater than that about the O–CH$_2$ bond. The higher barriers in the alkylthioalkyl radicals substantiate the view that there is greater delocalization of unpaired spin onto sulphur than onto oxygen.

Preferred Conformations of α-Alkylthioalkyl Radicals.—The magnitude of the β-proton coupling constant and its temperature dependence can be used to provide information about the preferred conformation of substituted alkyl radicals.[27] The low value of *a*(β-H) and its increase with increasing temperature (see Table 4) indicates that $CH_3OCH_2\dot{C}HSBu^t$ preferentially adopts the eclipsed conformation (**10**). This contrasts with $\dot{C}H_3\dot{C}HCH_2OCH_3$ which exists in the alternative staggered conformation (**11**) though $CH_3\dot{C}HCH_2OCF_3$ prefers the eclipsed conformation.[28] It is not possible at this stage to say whether this is a result of steric and/or electronic factors. The temperature dependence of the β-proton splittings in $PhCH_2\dot{C}HSBu^t$ and $PhCH_2\dot{C}HOCH_3$ suggest that these radicals, like $PhCH_2CH_2$·[29] lie in the staggered conformation (**12**; X = SBu^t and OCH$_3$). In contrast the radicals $Bu^tS\dot{C}HCH_2CH_2CH_2Ph$ and $Bu^tS\dot{C}HCH_2CH_2SBu^t$ also appear to adopt an eclipsed conformation.

Conclusion.—The magnitude of the hyperfine splitting constants in the 1-t-butylthioallyl and 3-t-butylthiopropynyl radicals indicates that the t-butylthio group is much more effective at delocalizing unpaired spin than is an alkoxy group. The same conclusion can also be reached from the barriers to rotation about the RXCH$_2$· bond in RSCH$_2$· and ROCH$_2$·.

Experimental

E.s.r. spectra were recorded with a Bruker ER200D or a Varian E-104 spectrometer on degassed samples, sealed in Spectrosil tubes, photolysed with light from a 500 W high-pressure mercury arc. Samples were examined in cyclopropane, toluene, t-butylbenzene, and/or di-t-butyl peroxide as solvent.

The sulphides were prepared by reaction of t-butyl mercaptan in sodium ethoxide with an equimolar proportion of the appropriate bromoalkane and were distilled prior to use.[30]

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